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## Report Title

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## Synthesis and Characterization of Perfluoro Quaternary Ammonium Ion Exchange Membranes for Fuel Cell Applications

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In this work alkaline exchange membranes were prepared from the 3M perfluorinated ionomer by functionalization with two amine species that were further alkylated to quaternary ammonium cations. The methyl amine polymer was successfully quaternized to produce an ion exchange capacity (IEC) of 0.72 meq g<sup>-1</sup>, while the isopropyl amine did not quaternize resulting a negligible IEC of 0.02 meq g<sup>-1</sup>. Membrane swelling under a range of humidity conditions was characterized before and after thermal annealing through small angle x-ray scattering. Swelling in the methyl cationic membrane was isolated to the ionic domain and showed little change by thermal annealing. The as-cast aminated isopropyl membranes exhibited inconsistent morphological ordering and hysteresis during humidity cycling. Thermal annealing of the isopropyl amine membrane induced structural reorganization that resisted change during humidity cycling. This work highlights the importance of morphology and thermal conditioning of ion exchange membranes to produce consistent long-term performance.

### Introduction

Proton exchange membrane (PEM) fuel cells have been a major research focus the last few decades due to their high power density and low emissions when operating with hydrogen fuel (1-3). Recently however, there has been increased interest in using alkaline fuel cells (AFCs) based on their potential for non-noble metal catalysts and ability to utilize complex fuels (2, 4-6). Current research on alkali fuel cells is primarily focused on the development of a solid polymer anion exchange membrane (AEM). While adequate hydroxyl conductivity has been demonstrated in AEMs under very wet conditions (7-9), conductivity rapidly diminishes at lower humidities. Better understanding of the role of water and polymer morphology on the ion conduction and stability of AEMs is necessary for practical AEM fuel cell development.

Perfluorosulfonic acid (PFSA) membranes have dominated the PEM fuel cell industry due to their high proton conductivity and sufficient chemical and mechanical stability (5, 10). For these reasons PFSA remain the benchmark comparison for all new PEMs and AEMs (1, 11). The performance and stability of PFSA, along with the vast literature available for comparison (12), has generated interest in development of a perfluorinated AEM based on the same polymer architecture. Several studies have synthesized perfluorinated AEMs (13-16), but reported stability and performance varies greatly.

The majority of PEM films have been shown to have a significant thermal history and require conditioning before steady state performance is obtained (17). One common annealing technique for polymers is thermal annealing where the membrane is brought above the glass transition temperature to increased chain mobility and allow polymer reorganization to a preferred orientation (18-21). Nafion™ exhibits a thermal transition around 110°C (12, 19, 22), so membranes are annealed at or above this temperature to improve conductivity performance. Thermal annealing induces morphological changes in the Nafion™ significantly affecting conductivity, transport, and water uptake in the film (18, 19, 23). It is expected that thermal annealing of perfluorinated AEMs will produce similar chain reorganization that affect swelling behavior and performance of the membranes.

In this work, a commercially produced perfluorinated ionomer was functionalized with two amine species and further alkylated to produce cationic, perfluoroquaternary ammonium (PFQA), polymers. Both amine species attached to the perfluorinated side chain, but only the smaller methyl amine was able to be alkylated to produce the methyl ammonium cationic polymer, PFMA. The larger, isopropyl amine did not quaternize to form a cation, resulting in an amine-functionalized perfluoropolymer, PFi-PA. Water uptake and swelling with humidity were examined in these polymer membranes. Structural reorganization by thermal annealing was investigated with in-situ small angle scattering experiments. The swelling behavior of the annealed membranes was compared with that of as-cast membranes to determine the effect of annealing on water uptake in the membranes. Unfortunately, degradation in hydroxide was observed for these membranes and further work would be needed to produce a stable cationic perfluorinated AEM.

## Experimental

Materials. The sulfonyl fluoride version of the perfluorinated ionomer at 800 EW was supplied in powder form by 3M Company. All other chemicals were purchased from Sigma Aldrich and were reagent grade.

Synthesis and Processing. The reaction scheme to synthesize the PFQA polymers was modified from that described in the patent by Matsui (24). In a typical synthesis the ionomer was dried overnight at reduced pressure (200 mbar) and 50°C. The ionomer (10 g) was swelled in anhydrous dimethylacetamide, ca. 25 cm<sup>3</sup>, decanted from molecular sieves, at a temperature of 100°C. The perfluorosulfonyl material was aminated using a 10-fold molecular excess of the diamine, 3-(dimethylamino)-1-propylamine for the PFMA and 2-(diisopropylamino)ethylamine for the PFi-PA. The solvent was removed and the polymer was treated with triethylamine (15 cm<sup>3</sup>) to completely remove the HF byproduct. The product was again dried in a rotovap before a 10-fold excess of the corresponding alkyl iodide was introduced to the reaction vessel to quaternize the terminal amine. The material was then dried and treated with a 5-fold excess LiCl in MeOH (25 cm<sup>3</sup>) overnight, followed by solvent removal and drying in a vacuum oven. The final product was separated from the excess LiCl by thoroughly washing in water, and a final drying step to give a light brown powder. The functionalized polymer species are given in Figure 1. The polymers were cast into membranes from DMAc on Teflon blocks and dried under reduced pressure (200 mbar) at 70°C, to give light brown films. The PFMA film was ca. 100 µm thick and brittle, particularly when dry. The PFi-PA membrane was ca. 200 µm thick and fairly flexible under both dry and wet conditions.

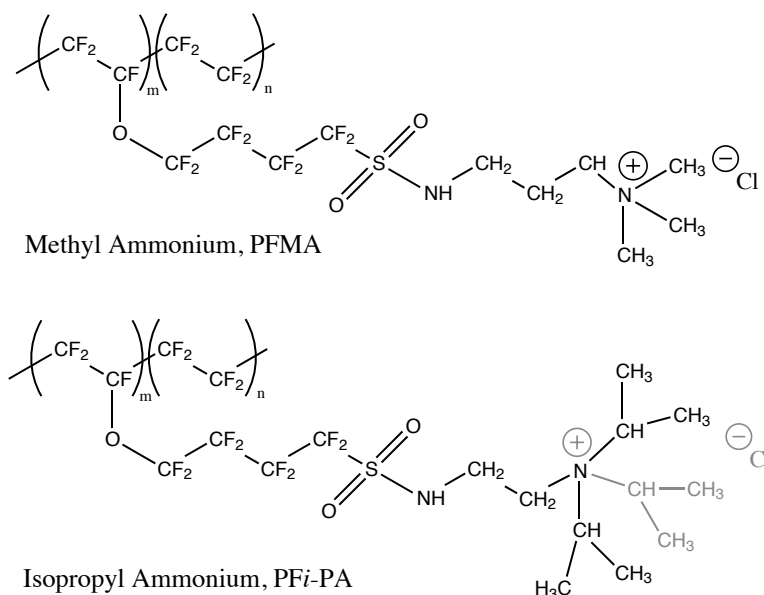


Figure 1. Chemical structure of the functionalized PFQA polymers. The PFMA membrane was alkylated to form the methyl ammonium cation. The PFi-PA did not quaternize to a significant degree remaining primarily as an amine species. The resulting structure of the PFi-PA is labeled in black; the grey bonds represent the expected structure if the material was alkylated to form a quaternary ammonium cation.

**Measurements.** FTIR spectra were obtained on a Nicolet Nexux 470 FT-IR ESP with an attached Specac Diamond Attenuated Total Reflectance (ATR) attachment. Typical spectrum range was  $4000\text{--}500\text{ cm}^{-1}$  with a resolution of  $4\text{ cm}^{-1}$  and 128 scans.

The ion exchange capacity of the material was determined by titrating the chloride ions in solution after soaking chloride form membranes in 1M sodium bicarbonate solutions for 48 hours. Standardized silver nitrate solution was used to titrate the membrane solutions with a potassium chromate indicator. The end point for the titration was defined as the point where permanent rust colored precipitates were seen in solution.

Water uptake was characterized using a SMS dynamic vapor sorption apparatus. A small membrane sample, ca.  $15\text{ mm}^2$ , was placed on a glass weigh plate and change in mass was measured gravimetrically under different humidity conditions. Humidity was cycled between dry and saturated conditions in steps of 20%RH. The water uptake (WU) of the membrane was calculated based on Equation [ 1 ]

$$\text{WU} = \frac{m_{\%RH} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \quad [ 1 ]$$

where  $m_{\%RH}$  is the mass of the sample at the given relative humidity and  $m_{\text{dry}}$  is the mass of the dry sample. The mass of the dry membrane was taken as the measured mass at the end of the initial four-hour drying period. The mass of the membrane was monitored as a function of time while incrementally changing the relative humidity.

Small angle x-ray scattering experiments were performed at The Basic Energy Sciences Synchrotron Radiation Center (BESSRC), beamline 12-ID-B, at the Advanced Photon Source at Argonne National Lab. Measurements were taken in a transmission geometry using a Pliatus 2M SAXS detector with an acquisition time of 1 s and an incoming x-ray wavelength of  $1\text{ \AA}$  with a beam energy of 12 keV. The 2D scatter was

radially integrated to obtain data of intensity versus scattering vector,  $q$ . The transmission intensity was normalized to exposure time and flux of the direct beam through the sample. However, because of the swelling of the samples tested, absolute thickness and atomic density could not be determined in-situ and the intensity units become arbitrary. A custom built four-sample oven controlled the humidity and temperature of the samples during scattering experiments. Typical experiments contained three membrane samples and one empty window so a background spectrum could be obtained throughout the scattering experiment. The humidity of sample environment was controlled using a combination of wet and dry nitrogen. Samples were removed from water, blotted dry and mounted on the sample holders using Kapton™ tape. Samples were inserted into the oven maintained at 60°C and 95% relative humidity. The samples were allowed to take up water for 20 minutes before x-ray spectra were taken. Humidity was then stepped down to 75%, 50%, 25%, and dry gas in 15-minute steps. After the dry step was completed, the humidity was set directly to 95% relative humidity for 15 minutes to test for hysteresis of the membranes. In-situ annealing experiments were performed by inserting membranes into the oven at 160°C for five minutes, cooling the samples to 60°C, followed by humidification and final drying of the samples at 60°C. SAXS spectra were taken throughout this cycle to determine polymer reorganization by thermal annealing.

## Results and Discussion

Characterization of the reaction progress and final reaction product were performed using a combination of FTIR and chloride titration. FTIR spectra were obtained for the precursor material and following the amination and quaternization reactions. The 3M-sulfonyl precursor material displayed broad absorbance peaks between 1300 and 1100  $\text{cm}^{-1}$  corresponding to the C-F bonds along the backbone and side chain. The precursor material also showed a distinct peak at 1470  $\text{cm}^{-1}$  that is associated with the S-F motion (25) or the asymmetric stretch of the  $\text{SO}_2\text{F}$  group (15). This peak is drastically reduced upon amination where the S-F bond is replaced by an S-N bond. The S-N bond produces new peak at 1375  $\text{cm}^{-1}$  (26). The peak at 1470  $\text{cm}^{-1}$  was not reduced completely suggesting incomplete reaction of the sulfonyl groups. The attachment of the diamine to the sulfonyl produces new peaks at 1650  $\text{cm}^{-1}$  corresponding to the N-H bond and 3000 and 2700  $\text{cm}^{-1}$  corresponding to the C-H bonds of the alkyl groups of the diamine. Figure 2 shows the spectra of the 3M precursor and the perfluorinated polymers following the quaternization reaction step. Quaternization of the material produces a broad peak between 3600 and 3000  $\text{cm}^{-1}$ , this is due to the O-H bond of water that coordinates with the cationic group following quaternization. The PFMA polymer displays the broad O-H peak centered at 3400  $\text{cm}^{-1}$ , however this peak is absent in the PFi-PA polymer suggesting the material was not quaternized to a significant degree. This result was confirmed by determination of the PFQA membrane IECs. The extent of quaternization, reflected by the IEC, was determined by chloride titration. The methyl ammonium material appeared to quaternize the fullest giving it an IEC of 0.72 meq  $\text{g}^{-1}$ , the theoretical value is ca. 1.0 meq/g. The isopropyl ammonium polymer did not quaternize to a significant degree as reflected by its low IEC, 0.02 meq  $\text{g}^{-1}$ . Initially, standard acid/base titrations, in which the membranes were exposed to 1M sodium hydroxide solution, were performed to determine IEC. But the acid/base titrations resulted in extremely low IEC values, almost three orders of magnitude lower than the chloride titration. It is believed the perfluorinated membranes were not stable in hydroxide

solution and resulted in complete loss of the cation groups that were washed away prior to the titration with acid.

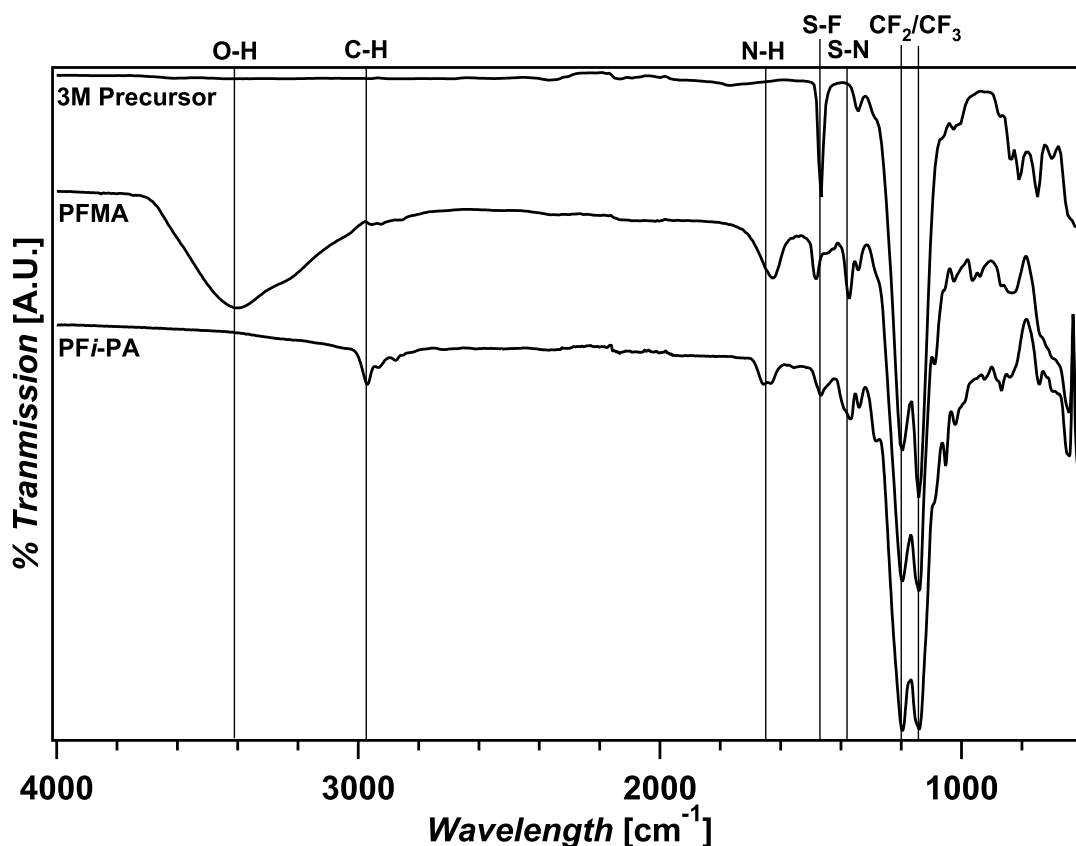


Figure 2. FTIR spectra for the 3M precursor material and the final quaternized PFMA and PFi-PA polymers. The important peaks are labeled to show the reduction of the S-F peak and addition of the N-H, S-N, and C-H peaks that signify the attachment of the amine species to the perfluorinated side chain. The broad O-H peak in the PFMA material is due to water association with the cation signifying quaternization, the PFi-PA material lacks this peak.

The level of quaternization in the PFQA membranes significantly influenced the level of water uptake by the membranes. The PFMA membrane had a total water uptake of 8wt%, compared to a very low level of water uptake by the PFi-PA membrane, 2.8wt%. The water contained in the PFMA membrane is associated with the cation groups, but because the PFi-PA membrane contains almost no cation groups it is expected that the water absorbed in the membrane has a different interaction with the polymer. This theory was further investigated by small angle x-ray scattering experiments of the as-cast PFQA membranes under different humidity conditions.

The dominant feature of the SAXS spectra for the PFMA material is a peak around  $0.15 \text{ \AA}^{-1}$ , Figure 3. This feature is similar to the “ionomer peak” of PFSA materials that corresponds to the ionic aggregates of the polymer where water will be contained for swollen membranes (27-29). The ionomer peak shifts to lower  $q$  as the humidity is increased due to the expansion of the ionic domain with water. The ionic region of the PFMA membrane increased by  $5 \text{ \AA}$  from a dry to humidified state. The PFi-PA membrane

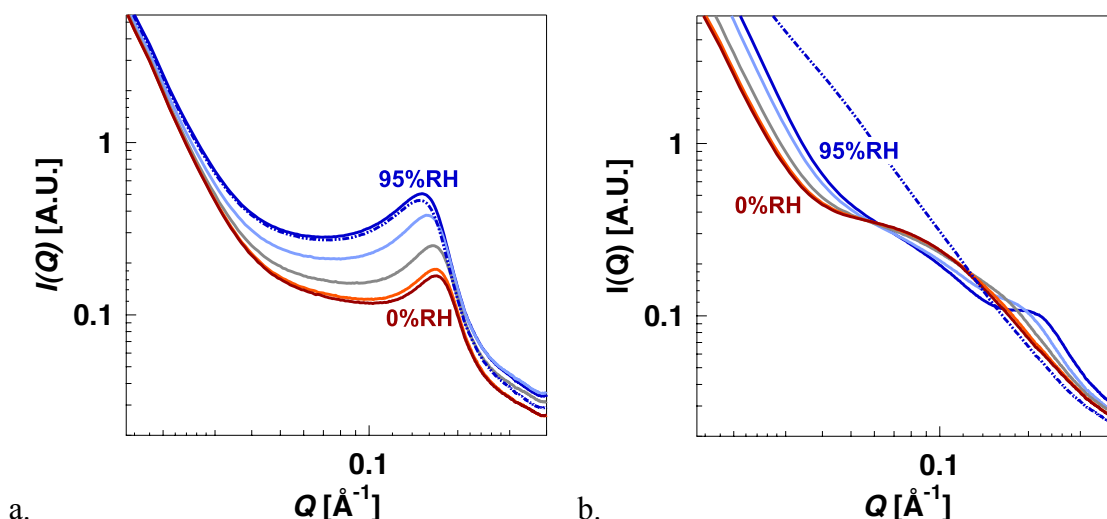


Figure 3. SAXS spectra of the as-cast a.) PFMA and b.) PFi-PA membranes at 60°C at saturated (dark blue) conditions transitioning to 75%RH (light blue), 50%RH (grey), 25%RH (orange), and dry conditions (red). The dashed lines represent the rehumidification of the membrane from a dry state. The PFMA membrane showed no hysteresis with humidity cycling while the PFi-PA membrane lost all scattering features upon rehumidification.

did not display a distinct “ionomer peak”, but rather had a range features suggesting different levels of structural ordering in the polymer, Figure 3. The humidified PFi-PA displays a slight shoulder at  $0.09 \text{ \AA}^{-1}$  and a more distinct shoulder at  $0.2 \text{ \AA}^{-1}$ , the same region as the PFMA ionomer peak. As the PFi-PA membrane dries, the broad shoulder around  $0.09 \text{ \AA}^{-1}$  becomes more distinct while the shoulder at  $0.2 \text{ \AA}^{-1}$  disappears. Upon rehumidification the PFi-PA membrane displayed significant hysteresis, losing all distinct scattering features, as shown by the dashed line in Figure 3b. The cation groups in the PFMA membrane confined swelling to the ionic region without significant structural changes in the polymer backbone, while the PFi-PA membrane, due to its lack of cation, had different levels of structural reorganization with hydration and did not maintain a consistent structure during humidity cycling.

Structural reorganization in the PFQA membranes was examined by annealing samples in-situ during SAXS acquisition, Figure 4. Thermal annealing produced no significant reorganization in the PFMA membrane. In similar experiments on PFSA membranes polymers, crystallinity increased following thermal annealing (30, 31). The absence of spectra changes in the PFMA membranes suggests that either the 160°C annealing temperature was not sufficient to induce crystallization or that the cation species somehow hindered the polymer reorganization. Humidity cycling of the annealed PFMA membrane at 60°C produced scattering very similar to the as-cast membrane tested previously, Figure 5. Thermal annealing produced significant structural reorganization of the PFi-PA in both the small range “amine” ordering and the long range backbone ordering, Figure 4. Both shoulders present in the PFi-PA spectra during the humidity experiments became more distinct during annealing and there was an iso-scattering point observed ca.  $0.3 \text{ \AA}^{-1}$ . The structural reorganization of the PFi-PA membrane was preserved during humidity cycling producing spectra with consistent



structural features under wet and dry states, unlike the as-cast membrane, Figure 5. The significant structural reorganization of the aminated PFi-PA membrane during annealing, compared to the negligible structural changes in the cationic PFMA membrane, suggests that the cation may restrain chain mobility preventing reorganization during thermal annealing.

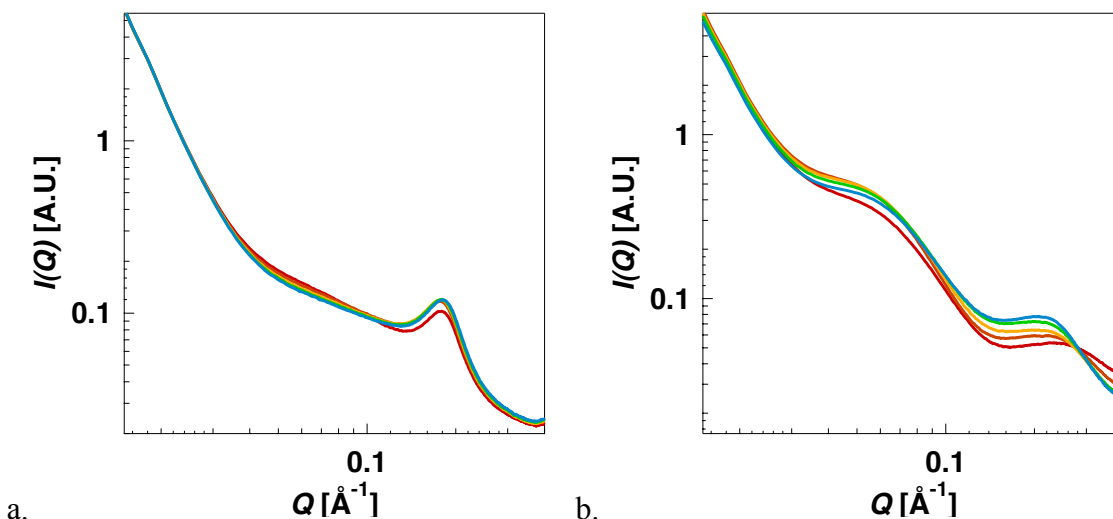


Figure 4. SAXS spectra of the a.)PFMA and b.)PFi-PA membranes during the annealing experiment. The spectra transition from the membranes at  $160^\circ\text{C}$  (red lines) cooling to  $60^\circ\text{C}$  (blue lines). The PFMA membrane showed little changes throughout the annealing experiment, while in the PFi-PA membrane the spectra shoulders became more distinct and there was an iso-scattering point observed ca.  $0.3 \text{ \AA}^{-1}$ .

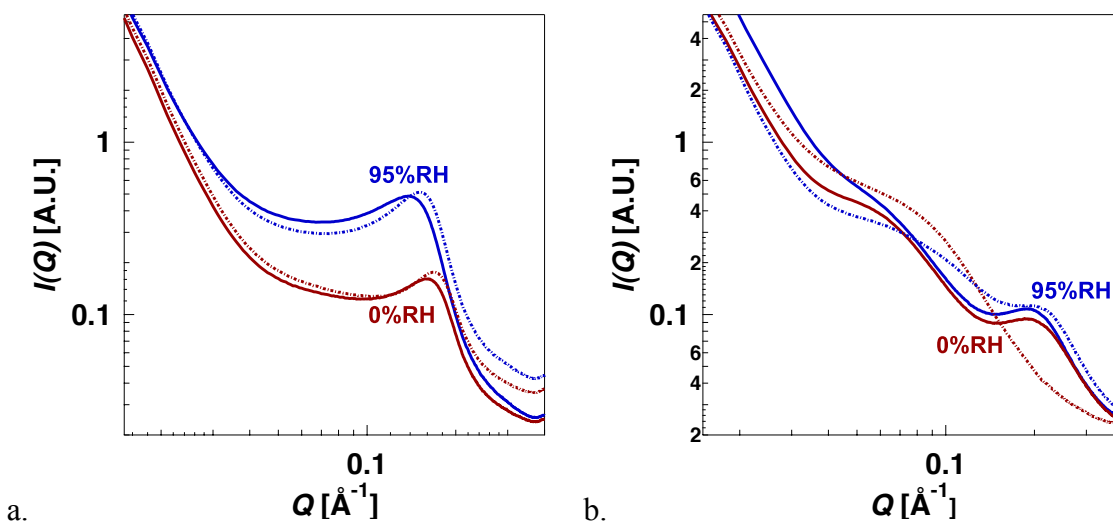


Figure 5. Comparison of the spectra for the as-cast (dashed lines) and the annealed (solid lines) membranes at saturated (black) and dry (grey) conditions of the a.)PFMA and b.) PFi-PA membranes. There was little difference between the as-cast and annealed membranes for the PFMA membrane. The PFi-PA annealed membrane spectra differed greatly from the as-cast sample, annealing produced structure that was consistent during humidity cycling unlike the as-cast membrane.

## Conclusions

In this work, a perfluorinated polymer was functionalized with two amine species that were further alkylated to produce cationic polymers as potential AEMs. The methyl amine polymer showed significant quaternization producing a cationic polymer, while the isopropyl amine did not quaternize to a significant degree resulting in very different behavior for the two polymers. Water uptake was almost four times higher for the PFMA membrane compared to the PFi-PA membrane. Small angle scattering experiments suggested the PFMA membrane had ionic aggregation and swelling similar to that of PFSA membranes and exhibited no major morphological reorganization during thermal annealing. Humidity cycling resulted in inconsistent morphological features and hysteresis in the as-cast PFi-PA membrane; however, thermal annealing of the membrane allowed chain reorganization that produced distinct scattering features that were no longer influenced by humidity cycling. The differences in annealing behavior of the aminated PFi-PA polymer compared to the quaternized PFMA polymer, suggests that the cation may restrict chain mobility and prevent reorganization during annealing. This study highlights the importance of understanding polymer reorganization by thermal treatment and morphological changes due to water swelling to produce stable anion exchange membranes.

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